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16. ABSTRACT

X-ray fluorescence (XRF) has become an effective technique for determining the elemental content of aerosol samples. For quantitative analysis, the aerosol particles must be collected as uniform deposits on the surface of Teflon membrane filters. An energy dispersive XRF spectrometer having a pulsed x-ray source that excites Ti, Mo, and Sm secondary targets has sufficiently low minimum detectable limits to enable 20 - 25 different elements to be detected and analyzed in atmospheric aerosol samples. For quantitative analysis using an energy dispersive spectrometer, the x-ray spectra are analyzed using a least squares procedure to eliminate interferences. Thin film standards are used to calibrate the spectrometer. Applications include the XRF analysis of 34,000 samples from the Regional Air Pollution Study in St. Louis.

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CHAPTER 1

X-RAY FLUORESCENCE ANALYSIS OF FILTER-COLLECTED AEROSOL PARTICLES

Thomas G. Dzubay

Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Dwight G. Rickel

Northrop Services Inc.
Research Triangle Park, North Carolina 27709

INTRODUCTION

To safeguard human health, a number of agencies are setting standards for acceptable levels of potentially harmful substances in airborne particulate matter. The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended standards for occupational exposure to numerous substances, including several toxic metals (ACGIH, 1973). California has a standard for lead in the ambient air. The U.S. Environmental Protection Agency (EPA) is investigating the need for air quality standards for lead and sulfur in atmospheric particulate matter. If such standards are ever applied on a nationwide basis, the capability to analyze large numbers of samples will be needed. Conventional analysis methods that require the sample to be in solution are not ideal for particles collected on filters because of the time-consuming sample extraction.

X-Ray fluorescence (XRF) has become an effective technique for determining the elemental content of aerosol samples. The primary advantage of this method is that 10-20 elements on each sample can be rapidly analyzed without performing a chemical extraction or destroying the sample. However, for this advantage to be realized, the sample must be in the form of a

uniform deposit on an appropriate type of membrane filter. The following sections discuss aerosol sampling, an XRF spectrometer, spectral analysis, calibration and attenuation.

AEROSOL SAMPLING

For quantitative XRF analysis, the aerosol particles need to be collected as a uniform deposit on a suitable filter medium. A filter medium of Teflon[1] is preferred because of the high purity and minimal tendency of Teflon to react with gaseous pollutants. Polycarbonate is also fairly good as a filter medium for the same reasons. Esters of cellulose have a high purity but are only useful as filter media for applications where the tendency to absorb moisture and to react with certain gaseous pollutants is not of concern. Most types of filters that contain glass or quartz contain large amounts of impurities of many elements, seriously limiting their application to XRF analysis.

Teflon membrane filters are available in a variety of forms. A thin 1-μm pore size Teflon membrane that is bonded to a polyethylene support net is available from Millipore Corporation as FALP Fluoropore,[2] and Liu and Kuhlmey (1977) report that its collection efficiency exceeds 99.9% for all particles in the 0.03-μm to 1-μm range. A minor problem with this type of filter is the difficulty of making a good vacuum seal in some types of filter holders. A Teflon membrane without a support net is available from Ghia Corporation, Pleasanton, California. This membrane has an asymmetric pore size distribution with 1-μm pores on one side and 10-μm pores on the other. When particles are collected on the 10-μm side, there is a tendency for submicron particles to penetrate into the filter. As a result, the filter medium attenuates the fluorescent X-rays from the particles, making it difficult to obtain quantitative results. Such attenuation is most pronounced for the lighter elements which emit soft X-rays. By collecting the particles in the 1-μm side, the particles are collected on the surface, which eliminates the attenuation by the filter.

In a typical XRF spectrometer, the exciting X-ray beam is nonuniform across the sample. Therefore, the aerosol deposit must be uniform if an accurate analysis is to be obtained. An acceptable deposit can be achieved if a filter holder with a suitable aerodynamic design is used.

A device called the dichotomous sampler is becoming widely used for atmospheric sampling (Dzubay and Stevens, 1975; Loo *et al.*, 1976; Dzubay *et al.*, 1977). It uses a virtual impactor to fractionate particles into respirable (< 3.5-μm) and nonrespirable (> 3.5-μm) fractions. The two fractions are collected as uniform deposits on membrane filters.

Another technique that achieves the same result is the use of two Nuclepore polycarbonate filters in series (Parker *et al.*, 1977). The first filter has 12-μm pores and collects the nonrespirable fraction; the second filter has 0.2-μm pores and collects the respirable fraction. Parker *et al.* (1977) have shown that the collection efficiency for the 12-μm filter closely matches the ACGIH criterion for removal of the nonrespirable fraction. This collection efficiency can be achieved for particles with a specific gravity of 1 when the flow rate and deposit area are 6.5 liter/min and 9.1 cm^2, respectively. However, the collection efficiency curve for the 12-μm pore size filter can change slightly as the specific gravity changes.

XRF SPECTROMETER

In an XRF spectrometer, the sample to be analyzed is excited by a beam of X-rays, which causes the removal of electrons from inner shells of the atoms in the sample. Such atoms may subsequently emit X-rays with wavelengths characteristic of the atoms. By resolving and counting the emitted X-rays, the amounts of the elements can be determined.

Both energy-dispersive and wavelength-dispersive systems are commonly used for resolving and counting X-rays (Birks and Gilfrich, 1976). In a wavelength-dispersive system, a crystal spectrometer resolves a spectrum of fluorescent X-rays into its various wavelength components (Jenkins and deVries, 1967). X-Rays of a specific wavelength are selected by a pair of slits and detected with a proportional counter of a scintillation detector. By moving the crystal and slits, the spectrum can be scanned to determine the amount of each element in the sample. Some systems are equipped with 16 or more crystal spectrometers to simultaneously determine the amounts of several elements in a sample (Wagman *et al.*, 1977).

A highly refined type of energy-dispersive XRF spectrometer is illustrated in Figure 1 (Goulding and Jaklevic, 1975). A lithium-drifted silicon type of solid-state detector with associated amplifiers and a multichannel analyzer is used to sort and record the emitted X-rays according to their energies. To obtain optimal sensitivity over a wide range of elements, the X-ray tube in Figure 1 does not excite the sample directly but excites it indirectly by means of secondary targets. Each sample is sequentially excited using three different secondary targets: titanium, molybdenum and samarium. Corresponding to each secondary target, the X-ray tube cathode is operated at potentials of -50, -60 and -80 kV, respectively. The anode of the X-ray tube is mounted close to the secondary target to provide adequate count rates at X-ray tube

[1] Registered trademark of E. I. duPont de Nemours & Company, Inc., Wilmington, Delaware.

[2] Mention of commercial products or company names does not constitute endorsement by the U.S. Environmental Protection Agency.

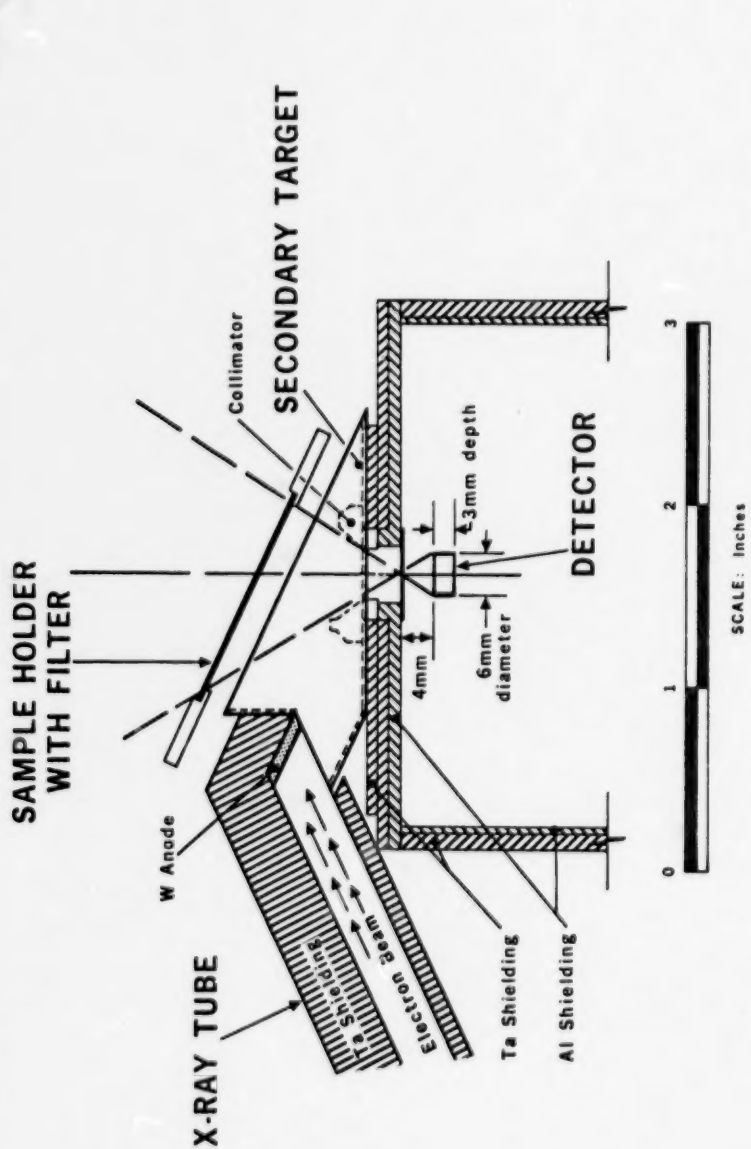

Figure 1. A cross-sectional view of an energy-dispersive XRF spectrometer that uses a low-power X-ray tube and interchangeable secondary targets for sample excitation.

power levels below 100 W. The X-ray tube is operated in a pulsed mode to minimize pulse pile-up losses and to obtain the maximum usable count rate (Jaklevic *et al.*, 1976).

For any application of an XRF spectrometer, the detection limits must be well below the concentrations to be measured. Figure 2 compares the detection limits of the energy-dispersive spectrometer with the range of urban atmospheric concentrations of elements (Cooper, 1973) and with the ACGIH threshold limit values (TLVs) for occupational exposure (ACGIH, 1973). The detection limits, C'_D, represent the ability of the spectromter to detect (at the 95% confidence level) a single element deposited on a Fluoropore membrane filter. The detection limits were calculated from the expression (Currie, 1977):

$$C'_D = 3.29\,(St)^{-1}\,[tR_b + (\epsilon tR_b)^2]^{1/2} \qquad (1)$$

where t = counting time for each fluorescer (100 sec)
R_b = background count rate about the full width at half maximum (FWHM) of each major peak (counts/sec)
S = sensitivity expressed in (counts/sec) per (ng/cm^2) for the FWHM region of the peak for each element
ϵ = 0.02, the assumed relative standard deviation for determining background with infinitely good counting statistics

To relate the detection limit scale on the right in Figure 2 to the concentration scale on the left, the detection limits must be multiplied by a sampling factor equal to the air volume sampled per unit area of filter. When the sampling factor is 1 m^3/cm^2, the detection limits plotted in Figure 2 can be read in ng/m^3; 20 to 25 elements can be detected in an urban atmosphere at this sampling factor (Figure 2). To monitor occupational exposures of elements having concentrations in the vicinity of the ACGIH TLVs, a sampling factor of 0.005 m^3/cm^2 provides sufficient sample for the XRF spectrometer. This sampling factor could be obtained for 8 hr of sampling at a flow rate of 80 mg/min through a 32-mm-diameter portion of a filter. The 80 mg/min flow rate is low enough that small samplers mounted on the worker's lapel could be used.

SPECTRAL ANALYSIS

From an X-ray spectrum of an unknown sample, one must extract the components that represent the amount of each element. When an energy-dispersive detector is used, the spectra can contain interferences from overlapping K_α, K_β, L and M X-ray lines. A variety of methods are available to analyze such spectra (Arinc *et al.*, 1976; Jaklevic *et al.*, 1974; Kaufmann *et al.*, 1976; Russ, 1977; Rickel and Dzubay, 1978). The least-squares method is one of the most promising approaches.

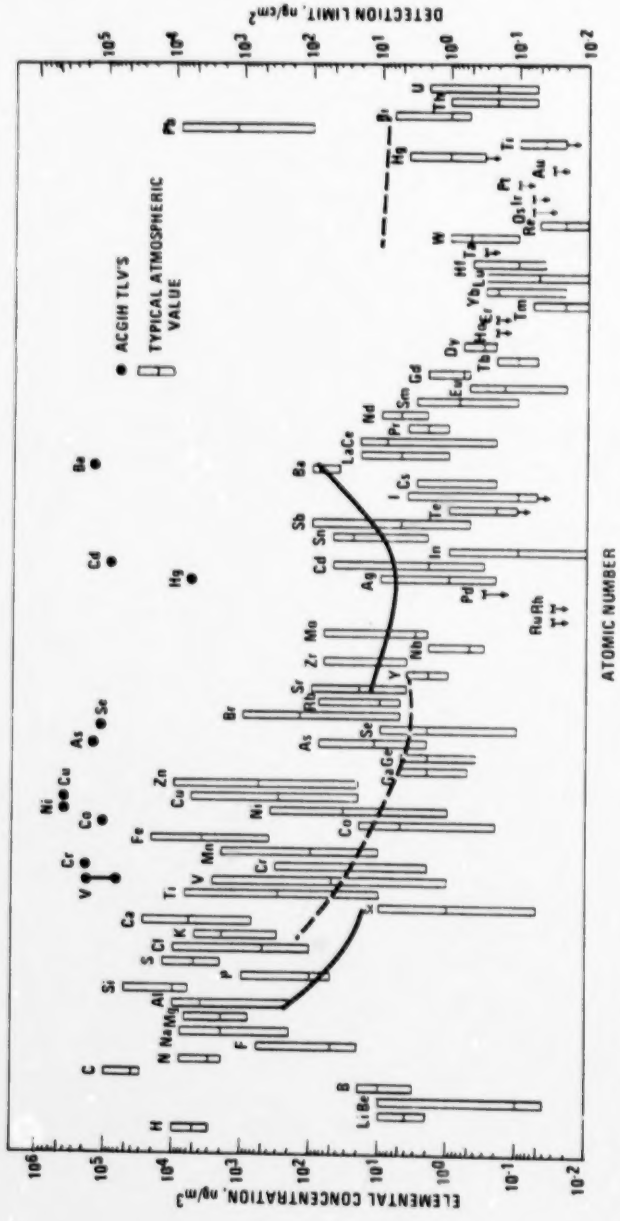

Figure 2. A comparison of the ranges of concentrations of elements in urban atmospheres (Cooper, 1973) and the minimum detectable limits for the energy-dispersive spectrometer described in the text. The minimum detectable limits are represented as dashed lines for the molybdenum secondary target and as solid lines for the titanium (left) and samarium (center) secondary targets. Also shown are occupational TLVs (ACGIH, 1973).

Using the least-squares method, a multielement spectrum is represented as a sum of pure element spectra. For this purpose, a library of spectra of pure element standards is recorded on magnetic tape and stored in a computer memory prior to the analysis of any unknown samples. The background is represented by a spectrum of a clean membrane filter. The least-squares method consists of finding the linear combination of pure element spectra (and background) that best describes the spectrum of the unknown sample. The amount of each elemental component in the spectrum is equivalent to the amount of each pure element standard needed in the linear combination.

Figure 3 illustrates the application of the least-squares method to a sample containing iron, cobalt, arsenic, lead and other elements. Figure 3a shows a spectrum of this sample analyzed using the molybdenum secondary target; figures 3b and 3c show a few of the 20 pure element spectra included in the library. Figure 3d shows the difference between the sample spectrum and the result of the least-squares fit; the differences are normalized by the standard deviations (σ) computed from Poisson statistics. The appropriateness of the model is indicated by the fact that the model fits the data within 3σ for nearly 100% of the points. The concentrations of the major components in the sample are shown in Figure 3a. The apparent interferences between the iron and cobalt peaks and the arsenic and lead peaks are adequately resolved.

We routinely use the least-squares method to analyze spectra from 20 to 200 samples per day. The mathematical computations are executed on a large computer which has to invert a 20 x 20 matrix for each spectrum that is analyzed. Rickel and Dzubay (1978) have found that by making a slight change in the least-squares method, the large matrix needs to be inverted only once. Thereafter, any number of spectra can be analyzed using relatively simple computations that can be executed on a minicomputer. Preliminary tests indicate that both weighting procedures give equivalent results.

CALIBRATION

After completing the spectral analysis for a sample, the concentrations (C_z) for each element can be computed from the expression:

$$C_z = Na_z/(F_zA_z) \qquad (2)$$

For each element, a_z is the number of counts in the spectrum determined by the least-squares method. A_z, which will be discussed in the next section, is an attenuation correction factor. F_z is a calibration constant for each element. For each secondary target in the XRF spectrometer, a normalization constant N is needed to account for the operational conditions of the spectrometer and is used to express the results in the desired units.

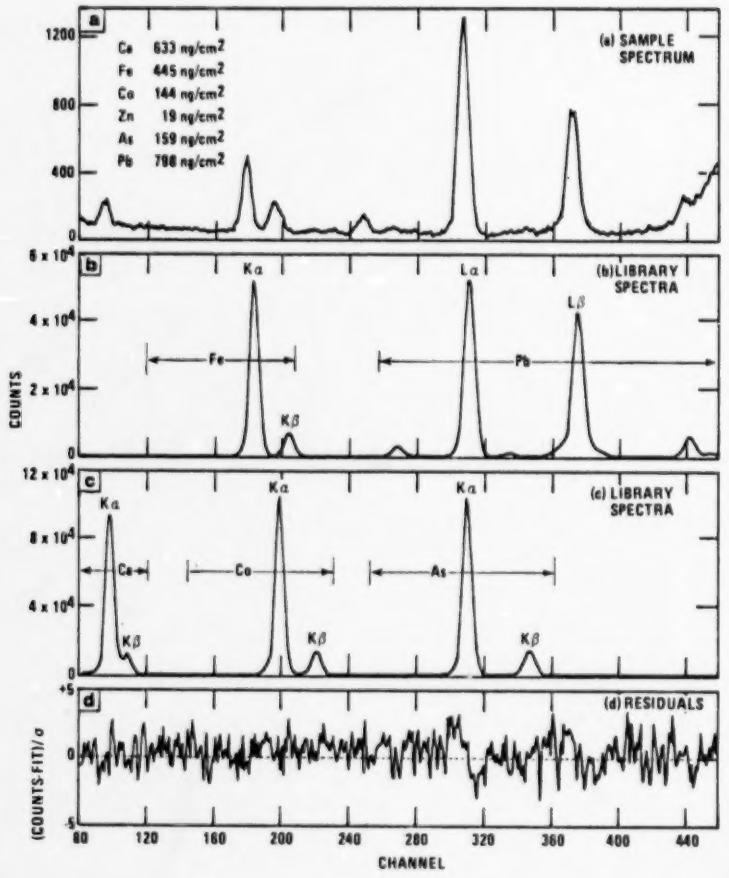

Figure 3. a. A spectrum for a multielement sample having interfering peaks.
b. Library spectra for iron and lead.
c. Library spectra for calcium, cobalt and arsenic.
d. Spectrum of residuals computed from differences between sample spectrum and the least-squares fit. The weight factor is $\sigma = \sqrt{\text{counts}}$.

A set of calibration standards is needed to determine the quantities N and F_z of Equation 2. The standards should be thin films that contain elements with a known mass per unit area. To eliminate possible errors due to any nonuniformity in the exciting X-ray beam, the standards must be uniform and should be similar in diameter to the unknown deposits being analyzed.

Figure 4 shows a calibration of the spectrometer using two different types of thin standards. The data plotted as circles (O) represent the F factors determined using dried solution standards obtained from Columbia Scientific Industries, Austin, Texas. These standards consisted of pairs of elements deposited in precisely known ratios of 1-mg/cm² Millipore filters. One element of each pair was always manganese or cadmium, making it possible to precisely determine the F factor relative to a common element. For the lighter elements an attenuation correction was made, ranging from the factor 0.46 for aluminum to 0.97 for titanium. The data in Figure 4 plotted as squares (□) were obtained using vacuum-evaporated deposits on thin mylar films, which were supplied by Micromatter Co., Seattle, Washington. Except for a few small discrepancies, the agreement between the two types of standards is very good for elements with atomic numbers above 15. For lighter elements, uncertainties in correcting for attenuation in the standards limit the accuracy.

A calibration based on standards can be improved by fitting a smooth curve to the measured F factors. Giauque *et al.* (1973) have shown that the calibration can be described by a formula that includes the basic parameters of the X-ray fluorescence process. The smooth curves in Figure 4 represent the product of Giauque's formula and a second-order polynomial. The terms of the polynomial are adjusted to give a best fit to the experimental calibration points. In this way, small errors in the standards are smoothed out. The smooth curves in Figure 4 are normalized to F = 1 for sulfur, copper and tin.

Determination of the normalization factors of Equation 2 requires uniform sulfur, copper and tin standards of precisely known mass per unit area. The sets of evaporated films and dried solution standards described above were consistent only within 10 to 15% in an absolute sense, even though Figure 4 shows them to be typically consistent to 5% or better in a relative sense. The lack of absolute agreement was explained by a systematic difference in the deposit profile between the two types of standards. Indeed, some of the vacuum-evaporated films appeared to be thicker at the center than at the edges.

A new type of standard is being developed. The Research Triangle Institue, in cooperation with EPA, is fabricating discs of plastic film containing known amounts of calibration elements. The discs are rugged and easy to handle, yet their 2-3 mg/cm² mass per unit area results in low X-ray absorption for elements with atomic numbers above 22. Initial experience indicates that the weight percent of the calibration elements in such standards can be accurately replicated (Dzubay *et al.*, 1977). Sets containing 20 elements are presently being fabricated.

Although the polymer standards are suitable for elements with atomic numbers above 22, they are too thick to be used as thin standards for lighter

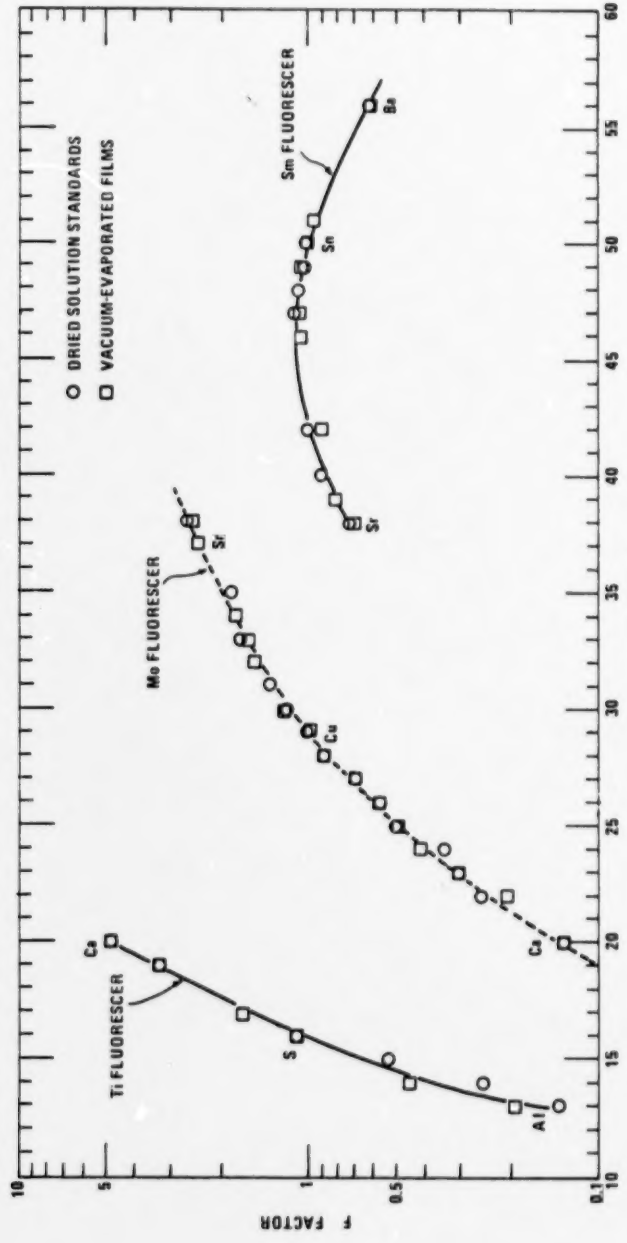

Figure 4. Calibration data (F factors) for K X-rays excited using titanium, molybdenum and samarium secondary targets.

elements. To determine the normalization factor for sulfur relative to the value for copper, deposits of copper sulfate particles are used. Such deposits are prepared by generating an aerosol of 0.2-μm copper sulfate ($CuSO_4 \cdot 5H_2O$) particles and collecting the particles on Fluoropore filters. Copper sulfate deposits prepared in a variety of thicknesses were analyzed by XRF (Figure 5). To obtain a calibration equivalent to a thin standard, the data in Figure 5 were fit with a straight line, which was extrapolated to zero deposit thickness. The sulfur calibration was adjusted so that the y-axis intercept was 0.505, which is equal to the sulfur-to-copper mass ratio for copper sulfate.

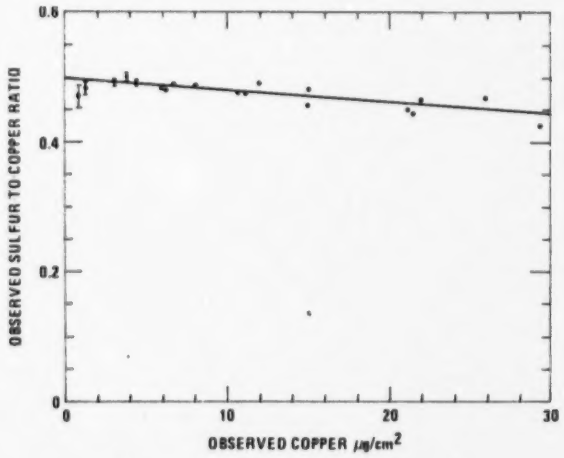

Figure 5. Ratio of sulfur and copper XRF yields for deposits of 0.2-μm copper sulfate particles. For zero deposit mass, the ratios are normalized to 0.505, which is the sulfur-to-copper mass ratio.

ATTENUATION

When thin calibration standards are used, it is necessary to make a correction for any attenuation of X-rays in the sample matrix. Both the exciting and fluorescent X-rays can be attenuated by the filter medium, by individual particles, and by layers of particles. The effects of attenuation tend to be the most pronounced for the lowest-energy X-rays.

Attenuation by the Filter

If particles are collected within the volume of a membrane filter, the X-rays are attenuated by the filter medium. To measure the magnitude of such

an effect, Loo *et al.* (1977) generated potassium sulfate and copper sulfate particles with various diameters in the 0.03-μm to 1-μm range and collected them on 1.2-μm pore size esters of cellulose filters (Millipore). By comparing the XRF yields for sulfur with the yields for potassium and copper, it was concluded that the attenuation factor for sulfur due to the filter was $A_F = 0.98 \pm 0.02$. For higher-energy X-rays from heavier elements, the attenuation factor for the filter would be essentially $A_F = 1$. Thus particles are collected at the surface of a filter even though they are much smaller than the pores of the filter. By using the copper sulfate technique described above for sulfur, any attenuation by the filter is implicitly accounted for.

If deliquescent particles are collected on a hydrophilic filter medium (such as esters of cellulose) in a humid atmosphere, the deposit can become moist and migrate into the filter medium to cause a serious attenuation problem for light elements (Liu *et al.*, 1978). Such migration can be minimized by collecting the particles on a hydrophobic filter such as Teflon. As an added precaution for excessively humid environments, a heater can be installed in the sampling stream to slightly warm the air and keep the relative humidity below 100%.

Layer Correction

If particles are collected on the surface of a filter as a layer, then the attenuation factor A is:

$$A = [1 - \exp - (\mu_L M/\Omega)]\, f/\mu_L M \qquad (3)$$

where M = average mass per unit area of the deposit
f = fraction of filter area covered by the particle deposit
μ_L = $\mu \sec\theta + \mu' \sec\theta'$
μ, μ' = mass absorption coefficients for incident and fluorescent radiation
θ, θ' = angles between sample normal and the incident and fluorescent X-ray paths

Equation 3 differs from a previously published expression (Dzubay and Nelson, 1975) because it includes a needed factor f. When filters are used to collect airborne particles, the deposit often has a noticeable grid pattern. For Fluoropore filters the support net causes such a grid pattern, and the factor f is equal to about 0.45.

The mass absorption coefficients in Equation 3 are given by:

$$\mu = \Sigma \mu_i W_i \qquad (4)$$

where μ_i and W_i are the mass absorption coefficients and mass fractions, respectively, for each individual element in the sample. Using the typical composition of the fine particle fraction of atmospheric aerosol (Dzubay and Nelson, 1974), one calculates $\mu_L = 0.56$ cm^2/mg for sulfur using the titanium

fluorescer of the spectrometer shown in Figure 1. As an example, a total loading of 0.2 mg/cm^2 on a Fluoropore filter, which is an exceptionally heavy loading, would require an attenuation correction of $A_L = 0.89$ for sulfur.

Attenuation within Particles

When the sample contains particles larger than a few micrometers, attenuation within the individual particles can be significant. For spheres of diameter d and density ρ, the attenuation factor A is given by:

$$A = \frac{3}{2Y^3}[Y^2 - 2 + (2Y + 2)\exp - Y]\exp(-kY\theta^2) \qquad (5)$$

where $k = 4 \times 10^{-6}$ (degrees)$^{-2}$
θ = angle between paths of exciting and observed X-rays
$Y = (\mu + \mu')\, d\rho$

Here μ and μ' are the mass absorption coefficients of the exciting and fluorescent X-rays, respectively. Equation 4 is appropriate for excitation of the sample with a monoenergetic beam of X-rays. The secondary target system shown in Figure 1 produces nearly monoenergetic X-rays. When the sample is excited with an X-ray source that has a broad range of energies, the attenuation must be averaged over that range of energies. Criss (1976) treats this problem and presents attenuation data for a wide range of particle types.

Figure 6 is a plot of the attenuation factor A vs the aerodynamic diameter calculated from Equation 5 for spheres containing various compounds of lead and tungsten. For excitation, a molybdenum secondary target and the geometry of Figure 1 are assumed. The aerodynamic diameter D is related to the geometric diameter d by:

$$D = \sqrt{S\, d} \qquad (6)$$

where S is the specific gravity. The aerodynamic diameter is used in Figure 6 because particles are classified by their aerodynamic properties in the human respiratory system and in certain aerosol sampling devices. Dzubay and Nelson (1975) report values of attenuation factors calculated from Equation 5 for a variety of particle types.

APPLICATIONS AND CONCLUSIONS

Rapid progress has been made during the past few years in the quantitative application of XRF to analyze aerosol samples. We have applied the techniques described above to measure particulate sulfur and have obtained excellent agreement with a new and precise ion chromatographic technique (Stevens *et al.*, 1978). Camp *et al.* (1975) have conducted an intermethod

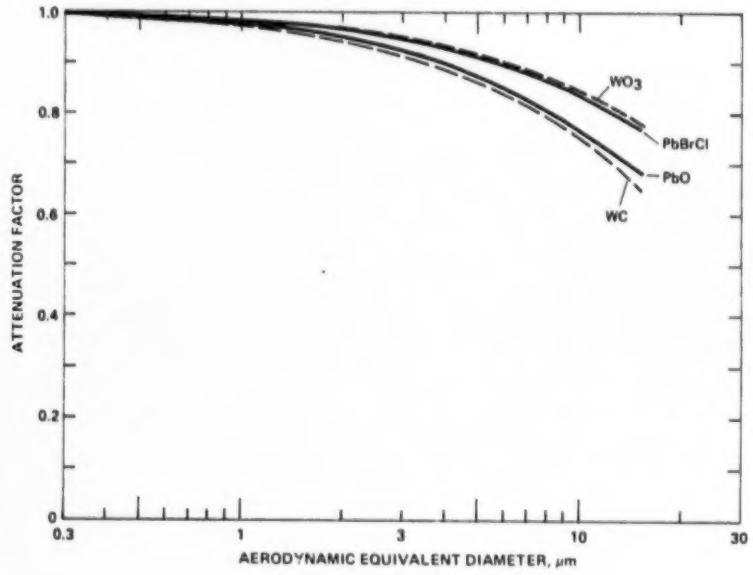

Figure 6. Attenuation factor vs aerodynamic equivalent diameter for various compounds containing lead and tungsten.

comparison using simulated and real aerosol samples and find very good agreement among several XRF laboratories. Such studies will be of continued importance as XRF becomes more highly refined and more widely used.

The energy-dispersive XRF spectrometer described in Figure 1 has been used to analyze 34,000 aerosol samples collected in St. Louis, Missouri, as a part of the Regional Air Pollution Study (RAPS) (Myers and Reagan, 1975; Loo *et al.*, 1978). Between 1975 and 1977, ten automated dichotomous (Loo *et al.*, 1976) samplers were continuously operated at flow rate of 50 liters/min in the St. Louis area to collect particles in both the fine (0-2.4 μm) and coarse (2.4-15 μm) size ranges for sampling periods ranging from 2 to 12 hours. Table I shows the concentrations of 23 elements measured by XRF and the total mass measured by beta ray attenuation (Goulding *et al.*, 1975) for a 12-hour sampling period on June 27, 1975. Data on the fine fraction are shown for all ten sites; data on the course fraction are shown for three representative sites. For RAPS sites 103 and 105, the sampling interval was 6 hours, and the data in Table I represent a pair of 6-hour measurements. For the 6-hour sampling period, the air volume sampled per unit area of filter was 2.5 m^3/cm^2; for the 12-hour sampling period at the other sites this factor was 5 m^3/cm^2.

Table I. Mass and Elemental Concentrations for Fine and Course Particle Aerosol Fractions Collected in Automated Dichotomous Samples that were Simultaneously Operated at 10 Different RAPS Stations in the St. Louis Area from Midnight to Noon of June 27, 1975

	Fine Fraction (<2.4 μm) (ng/m³)										Coarse Fraction (>2.4 μm) (ng/m³)			
Site/Element	103[a]	105[a]	106[b]	112[b]	120[b]	108[c]	115[c]	118[c]	122[d]	124[d]	106	112	124
Mass	56,000		47,000	54,000	51,000	43,000	47,000	38,000	36,000	39,000	35,000	33,000	39,000
Al	<260	<260	<130	<130	<130	<130	<130	<130	<130	<130	1190	1250	1260
Si	220	370	280	400	230	230	140	160	120	180	4700	5080	7070
P	40	85	<20	<20	<20	<20	<20	<20	<20	<20	260	310	350
S	6000	7700	6200	5700	5700	4300	5600	4350	3900	4600	1000	1060	660
Cl	160	180	50	210	190	55	150	100	56	80	350	275	250
K	230	240	200	161	180	240	155	120	103	150	420	460	510
Ca	95	150	120	90	67	110	50	90	30	150	2750	2200	1570
Ti	95	140	130	180	140	55	46	10	26	<7	560	1070	140
V	11	12	12	19	15	6	11	7	<5	<5	9	16	<5
Cr	14	6	9	6	10	16	<3	<3	<3	<3	11	36	9
Mn	18	28	26	19	63	14	15	6	5	7	39	50	22
Fe	300	410	300	320	280	250	160	72	87	82	1370	2140	740
Ni	10	13	5	5	5	3	3	<1	<1	<1	6	9	3
Cu	45	98	69	44	29	31	53	33	9	1	27	32	<1
Zn	120	420	290	120	230	65	160	20	88	17	150	82	4
Se	4	8	7	6	3	3	7	5	4	32	1	0	1
Br	216	180	140	200	170	190	71	29	23	25	49	74	3
Sr	<3	<3	<1	<1	<1	<1	<1	<1	<1	<1	6	7	4
Cd	<6	15	8	4	<3	<2	<3	20	<3	<3	<3	<3	<3
Sn	15	30	24	14	6	12	21	<3	5	<3	<3	<3	<3
Sb	<8	<8	<4	7	<4	6	<4	<4	<4	<4	<4	<4	<4
Ba	51	69	72	97	100	22	20	<10	<10	<10	59	78	22
Pb	1070	1140	1010	1120	970	960	560	500	230	150	200	280	31

[a]Heavy urban industrial.
[b]Urban St. Louis.
[c]Rural agriculture industrial.
[d]Rural agricultural.

The sums of the fine and coarse particle concentrations in Table I are consistent with the ranges of urban concentrations shown in Figure 2. When one takes into account the sampling volume per unit area factors, the list of elements in Table I is consistent with the predicted detectability shown in Figure 2. In addition to the data shown in Table I, arsenic, rubidium and mercury were also measured, but their concentrations did not significantly exceed the minimum detectable limits.

A striking feature appears in Table I when one compares the urban sites with the rural sites 122 and 124, located about 40 km to the north and 40 km to the south of St. Louis, respectively. Whereas the sulfur concentrations at the rural sites amount to at least 50% of the urban values, the concentrations of titanium, manganese, iron, nickel, bromine, tin, barium and lead decrease far more rapidly as the rural sites are approached. Thus, in contrast to the other elements, it appears that particulate sulfur has important sources that lie well beyond the urban area. The data on all 34,000 samples are presently being analyzed to provide information on the transport of sulfur and other elements in the St. Louis area.

Table II represents the application of XRF to samples collected in the wet grinding area of a tungsten processing plant. A pair of Nuclepore filters were

Table II. Concentrations of Elements in a Tungsten Processing Plant Collected Using a Series of Filter Sampling Techniques

Element	Respirable ($\mu g/m^3$)	Nonrespirable ($\mu g/m^3$)
Fe	12	7
Co	451	234
W	1850	838

operated in series (11-μm pore size) to collect the respirable and nonrespirable fractions (Parker *et al.*, 1977). It is clear that the cobalt concentration in Table II exceeds the occupational TLV of 100 $\mu g/m^3$ (ACGIH, 1973). This contrasts with the data in Table I for St. Louis, which show that the concentrations of all elements but lead are at least 1000 times lower than the occupational TLVs. For lead in St. Louis, the concentrations are typically 150 times lower than the occupational TLVs.

In the above applications, the nondestructive and multielement capabilities of XRF were of great importance. In the RAPS study, it would have been prohibitively costly to analyze 34,000 samples by methods that require extraction. In analyzing the samples from the tungsten processing plant, the XRF analyst was not instructed to find cobalt, yet the multielement

capability of XRF and the least-squares procedure facilitated its detection and analysis. This experience indicates that the XRF method is well suited to monitoring elemental concentrations on collected aerosol samples.

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